Prediction of properties of organic ferroelectrics and piezoelectrics by first-principles calculation

Shoji ISHIBASHI
National Institute of Advanced Industrial Science and Technology (AIST)
Tsukuba, Ibaraki 305-8568

For the 2,5-dihydroxybenzoic acid (DHBA) crystal, two possible switching mechanisms have been noted recently [1]. One is a flip-flop (FF) motion of hydroxy groups, and the other is inter-molecular proton transfer (PT). In Fig.1, structural snapshots of hydroxy groups in both the processes together with Berry phase variation [2]. λ and λ' are parameters to describe the FF and PT processes, respectively. $\lambda = +1$ and $\lambda' = +1$ correspond to the same target ferroelectric structure. The polarization-inverted structure in the PT process is described as $\lambda' = -1$ and its phase differs by 2π from that of $\lambda = -1$ reflecting the proton movements at the hydroxy groups. The Berry phase variation shows that the sign of the polarization-vector component differs between the two processes. The direct piezoelectric coefficient is evaluated, adjusting the polarization-vector component to be positive, from its change upon applying stress. The converse piezoelectric coefficient is evaluated by adjusting the sign of the electric-field component to be the same as that of the polarization-vector component. On the other hand, small structural changes are expected under a stress or an electric field. The change in polarization as a vector is uniquely defined and independent of the switching mechanism. Hence, the switching modes can be distinguished.

Using the QMAS code, we have performed computational simulations of the direct and converse piezoelectric effects for DHBA and also for Hdabco-ReO_4. By comparison with the experimental results, it is concluded that DHBA employs the FF process for its switching mechanism, whereas Hdabco-ReO_4 adopts the PT process.

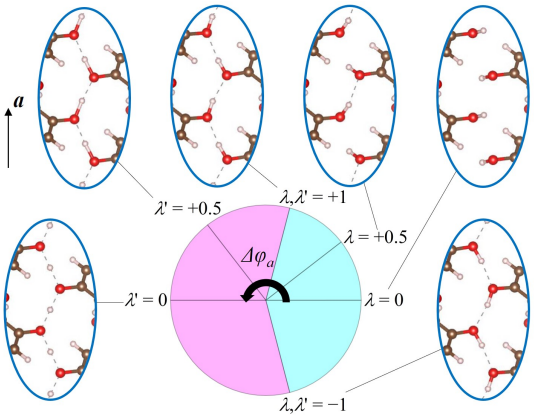

Figure 1: Berry phase variation ($\Delta\phi_a$) and structural snapshots of hydroxy groups during ferroelectric switching in the FF (λ) and PT (λ') processes for DHBA (S. Ishibashi, R. Kumai, and S. Horiuchi, Sci. Rep. **13**, 8810 (2023), DOI: 10.1038/s41598-023-34923-0).

References

[1] Y. Shimoi, S. Tsuzuki, R. Kumai, M. Sotome, and S. Horiuchi, J. Mater. Chem. C **10**, 10099 (2022).

[2] S. Ishibashi, R. Kumai, and S. Horiuchi, Sci. Rep. **13**, 8810 (2023).